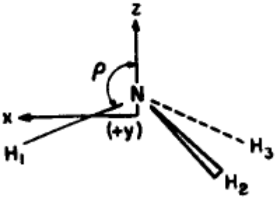
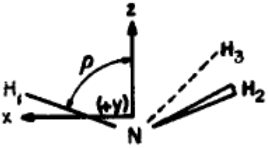
# Group theory and molecular spectroscopy.
## II. Ammonia molecule

We determine the symmetry of the $NH_3$ eigenstates with respect to permutations of H atoms.

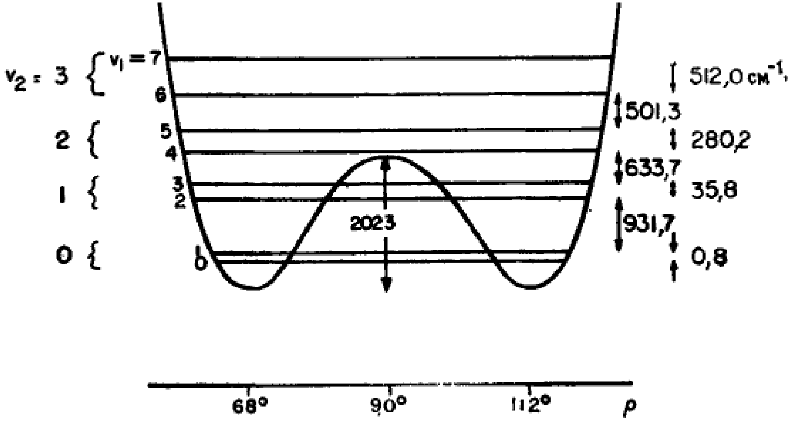


(a)



(b)

Key feature: resolvable inversion splitting.
It is therefore convenient to consider $NH_3$ as
a flat molecule with a strongly anharmonic vibrational DoF.


v2 = 3
v1 = 7
6
2
5
4
1
3
2
0
0
512,0 cm-1,
501,3
280,2
633,7
35,8
931,7
0,8
2023
68°
90°
112°
ρ

# Co-ordinate system and its transformations after permutations of H atoms

- Center of mass = origin
- Enumerate H atoms: 1, 2, 3
- $z$ axis: $\perp$ to the plane containing H atoms, right-screw oriented for #1 $\longrightarrow$ #2 $\longrightarrow$ #3
- $x$ axis: atom H #1 is in the $(x, z)$-plane
- $y$ axis: co-ordinate system is right-handed

$$\Psi = \Psi_e \otimes \Psi_v \otimes \Psi_r \otimes \Psi_I$$

The electronic ground state of ammonia is fully symmetric w.r.t. permutations of H atoms.

# Transformation of the Euler angles

$$e: \quad (\phi,\theta,\chi) \mapsto (\phi,\theta,\chi)$$

$$(123): \ (\phi,\theta,\chi) \mapsto (\phi,\theta,\chi + \tfrac{2\pi}{3})$$

$$(132): \ (\phi,\theta,\chi) \mapsto (\phi,\theta,\chi - \tfrac{2\pi}{3})$$

$$(23): \quad (\phi,\theta,\chi) \mapsto (\phi+\pi,\pi-\theta,-\chi)$$

$$(13) = (23)(132): \quad (\phi,\theta,\chi) \mapsto (\phi+\pi,\pi-\theta,-\chi + \tfrac{2\pi}{3})$$

$$(12) = (23)(123): \quad (\phi,\theta,\chi) \mapsto (\phi+\pi,\pi-\theta,-\chi - \tfrac{2\pi}{3})$$

# Transformation of rotational wave function

$$\Phi^J_{MK}(\phi,\theta,\chi) = e^{iM\phi} d^J_{MK}(\theta) e^{iK\chi}$$

$$\begin{aligned}
e: &\quad \Phi^J_{MK} \mapsto \Phi^J_{MK} \\
(123): &\quad \Phi^J_{MK} \mapsto e^{2\pi Ki/3}\Phi^J_{MK} \\
(132): &\quad \Phi^J_{MK} \mapsto e^{-2\pi Ki/3}\Phi^J_{MK} \\
(23): &\quad \Phi^J_{MK} \mapsto (-1)^J \Phi^J_{M\,-K} \\
(13): &\quad \Phi^J_{MK} \mapsto (-1)^J e^{2\pi Ki/3}\Phi^J_{M\,-K} \\
(12): &\quad \Phi^J_{MK} \mapsto (-1)^J e^{-2\pi Ki/3}\Phi^J_{M\,-K}
\end{aligned}$$

# $J$ = const, $M$ = const, $K$ is varied

$\underline{K=0}$: $\Phi^J_{M0}$ transforms according to an IR of the $S_3$ group.
This IR corresponds to the Young diagram:
$\{3\}$, if $J$ is even,
$\{1,1,1\}$, if $J$ is odd.

$\underline{K\neq 0}$: degenerate states $\Phi^J_{MK}$ and $\Phi^J_{M\,-K}$ transform according to a certain (reducible or irreducible) representation of $S_3$.

$\underline{K \bmod 3 = 0}$: reducible representation, $\{3\}\bigoplus\{1,1,1\}$.

$$\{3\}: \qquad \frac{1}{\sqrt{2}}[\Phi^J_{MK} + (-1)^J\Phi^J_{M\,-K}]$$

$$\{1,1,1\}: \qquad \frac{1}{\sqrt{2}}[\Phi^J_{MK} - (-1)^J\Phi^J_{M\,-K}]$$

$\underline{K \bmod 3 = \kappa, \text{ where } \kappa = 1,\ 2 :}$ transform. matrices for $\begin{pmatrix} \Phi^J_{MK} \\ \Phi^J_{M\,-K} \end{pmatrix}$

$$e \sim \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (12) \sim (-1)^J \begin{pmatrix} 0 & e^{2\pi\kappa i/3} \\ e^{-2\pi\kappa i/3} & 0 \end{pmatrix}$$

$$(13) \sim (-1)^J \begin{pmatrix} 0 & e^{-2\pi\kappa i/3} \\ e^{2\pi\kappa i/3} & 0 \end{pmatrix} \quad (23) \sim (-1)^J \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$(123) \sim \begin{pmatrix} e^{2\pi\kappa i/3} & 0 \\ 0 & e^{-2\pi\kappa i/3} \end{pmatrix} \quad (132) \sim \begin{pmatrix} e^{-2\pi\kappa i/3} & 0 \\ 0 & e^{2\pi\kappa i/3} \end{pmatrix}$$

Characters of the classes $\chi(e) = 2, \quad \chi(12) = 0, \quad \chi(123) = -1$

show that $\kappa = 1, 2$ corresponds to the IR $\{2, 1\}$.

# Vibrational states

For a $n$-atomic molecule, vibrational DoFs are given by (small) displacements $\delta \mathbf{r}_j$ of nuclei from the classical equilibrium positions, whereby

- Center-of-mass motion is excluded:

$$\sum_{j=1}^{n} m_j \delta \mathbf{r}_j = 0$$

- 3D rotations are excluded:

$$\delta \mathbf{r}_j [\mathbf{e}_\alpha \times \mathbf{r}_j] = 0, \qquad j = 1, 2, \ldots, n, \quad \alpha = x, y, z$$

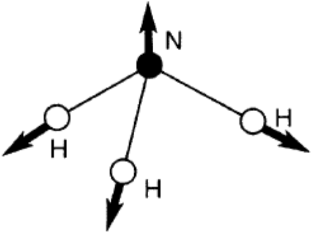
To the lowest order, separation of variables in normal coordinates. If a molecul contains identical nuclei, the vibrational states transform acccording to IRs of the permutation group. If the dimension $s$ of the respective IR is $> 1$, then the vibration frequency is $s$-fold degenerate.

# Normal vibrational modes of ammonia

$3 \times 4 - 3 - 3 = 6$ vibrational DoFs.

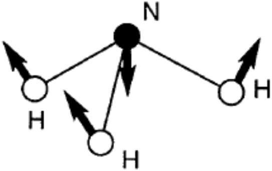
Non-degenerate normal modes

Young diagram: $\{3\}$



$\omega_1 = 3323 \text{ cm}^{-1}$

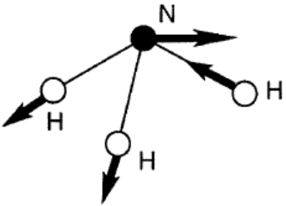
$\{1, 1, 1\}$



Anharmonic vibrations including inversion splitting. Energy distance between the two lowest inv. doublets $\approx 950 \text{ cm}^{-1}$

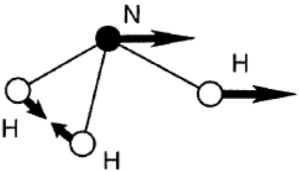
Doubly degenerate normal modes

Young diagram: $\{2, 1\}$



$\omega_3 = 3443\ \text{cm}^{-1}$

$\{2, 1\}$



$\omega_4 = 1627\ \text{cm}^{-1}$

In total $1 + 1 + 2 + 2 = 6$ vibrational DoFs.

Figures from McGinnis et al., Surface Sci. **494**, 28 (2001)

$$\Psi_v = \Phi_1(q_1)\Phi_2(q_2)\Phi_3(\vec{q}_3)\Phi_4(\vec{q}_4)$$

$\Phi_1$ and $\Phi_2$ are fully symmetric against permutations of H atoms, regardless of the vibrational quantum numbers $v_1$ and $v_i$ (or $v_2$ and upper/lower inversion doublet component).

The normal modes 3 and 4 are 2D oscillators,

$$\vec{\hat{b}}_l^{\dagger} = \tfrac{1}{\sqrt{2}}\left(\frac{\vec{q}_l}{a_l} - a_l \nabla_{\vec{q}_l}\right), \qquad l = 3, 4.$$

$$\hat{P} b_{l,i}^{\hat{\dagger}} = \sum_{i'=1}^{2} \tau(\hat{P})_{ii'} b_{l,i'}^{\hat{\dagger}}, \qquad i = 1, 2.$$

The state of the $l$th mode with the energy $\hbar\omega_l(v_l + \frac{1}{2})$ is $(v_l + 1)$-degenerate:

$$\Phi_l^{[k, v_l - k]} = \frac{1}{\sqrt{k!(v_l - k)!}} \hat{b}_{l,1}^{k\,\dagger} \hat{b}_{l,2}^{(v_l - k)\,\dagger} |0\rangle, \quad k = 0, 1, 2, \ldots, v_l.$$

The ground vibrational state is symmetric, $\forall \hat{P}: \ \hat{P}|0\rangle = |0\rangle$, i.e., $\{\lambda\} = \{3\}$.
The 1st excited state ($v_l = 1$) has the same symmetry type as $\vec{q}_l$, in the case of $NH_3$ $\quad \{\lambda\} = \{2, 1\}$.
For $v_l > 1$, the linear space spanned by $\Phi_l^{[k, v_l - k]}$ is a reducible representation of the permutation group.
There are $m_{\{\lambda\}}$ subspaces of functions transformed according to the IR $\{\lambda\}$.
Since characters of IRs of the group $S_n$ are real,

$$m_{\{\lambda\}} = \frac{1}{n!} \sum_P \chi^{\{\lambda\}}(P)\chi(P) = \frac{1}{n!} \sum_K \mathcal{N}_K \chi^{\{\lambda\}}(K)\chi(K),$$

where $\mathcal{N}_K$ is the number of elements in the class $K$, $\qquad \sum_K \mathcal{N}_K = n!$ .
For $NH_3$ $\quad n = 3$.

# Recalling classes of $S_3$

| $K$ | $e$ | $(ij)$ | $(ijk)$ |
|---|---|---|---|
| $\mathcal{N}_K$ | 1 | 3 | 2 |
| $\chi^{\{3\}}(K)$ | 1 | 1 | 1 |
| $\chi^{\{2,1\}}(K)$ | 2 | 0 | $-1$ |
| $\chi^{\{1,1,1\}}(K)$ | 1 | $-1$ | 1 |

# Transformation matrices of the {2, 1} IR

They determine transformation of $\begin{pmatrix} \hat{b}^\dagger_{l,1} \\ \hat{b}^\dagger_{l,2} \end{pmatrix}$

$$e \sim \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (23) \sim \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \begin{matrix} (12) \\ (13) \end{matrix} \sim \begin{pmatrix} 0 & e^{\pm 2\pi i/3} \\ e^{\mp 2\pi i/3} & 0 \end{pmatrix}$$

$$\begin{matrix} (123) \\ (132) \end{matrix} \sim \begin{pmatrix} e^{\pm 2\pi i/3} & 0 \\ 0 & e^{\mp 2\pi i/3} \end{pmatrix}$$

## $v_l = 2$

Transformation matrices for

$$\begin{pmatrix} \Phi_l^{[2,0]} \\ \Phi_l^{[1,1]} \\ \Phi_l^{[0,2]} \end{pmatrix} = \begin{pmatrix} (1/\sqrt{2})\, \hat{b}_{l,1}^{\dagger\,2}|0\rangle \\ \hat{b}_{l,1}^{\dagger}\hat{b}_{l,2}^{\dagger}|0\rangle \\ (1/\sqrt{2})\, \hat{b}_{l,2}^{\dagger\,2}|0\rangle \end{pmatrix}$$

$$e \sim \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (23) \sim \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\begin{matrix} (12) \\ (13) \end{matrix} \sim \begin{pmatrix} 0 & 0 & e^{\mp 2\pi i/3} \\ 0 & 1 & 0 \\ e^{\pm 2\pi i/3} & 0 & 0 \end{pmatrix} \quad \begin{matrix} (123) \\ (132) \end{matrix} \sim \begin{pmatrix} e^{\mp 2\pi i/3} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{\pm 2\pi i/3} \end{pmatrix}$$

Characters for classes:

$$\chi(e) = 3, \qquad \chi[(ij)] = 1, \qquad \chi[(ijk)] = 0.$$

$$m_{\{3\}} = (1 \cdot 3 \cdot 1 + 3 \cdot 1 \cdot 1 + 2 \cdot 0 \cdot 1)/6 = 1$$

$$m_{\{2,1\}} = [1 \cdot 3 \cdot 2 + 3 \cdot 1 \cdot 0 + 2 \cdot 0 \cdot (-1)]/6 = 1$$

$$m_{\{1,1,1\}} = [1 \cdot 3 \cdot 1 + 3 \cdot 1 \cdot (-1) + 2 \cdot 0 \cdot 1]/6 = 0$$

The linear space spanned by $\Phi_l^{[2,0]},\ \Phi_l^{[1,1]},\ \Phi_l^{[0,2]}$ has the structure

$$\{3\} + \{2, 1\}$$

Since all permutations are products of pairwise permutations, it is enough to consider only (*ij*) for construction of a wave function being transformed according to a certain $\{\lambda\}$.

$$\{3\} :\ \Phi_l^{[1,1]}, \qquad \{2, 1\} : \left( \begin{array}{c} \Phi_l^{[0,2]} \\ \Phi_l^{[2,0]} \end{array} \right).$$

Analogously, for $v_l = 3$, the characters are

$\chi(e) = 4, \qquad \chi[(ij)] = 0, \qquad \chi[(ijk)] = 1,$

$m_{\{3\}} \quad = (1 \cdot 4 \cdot 1 + 3 \cdot 0 \cdot 1 + 2 \cdot 1 \cdot 1)/6 \qquad = 1$

$m_{\{2,1\}} \quad = [1 \cdot 4 \cdot 2 + 3 \cdot 0 \cdot 0 + 2 \cdot 1 \cdot (-1)]/6 = 1$

$m_{\{1,1,1\}} = [1 \cdot 4 \cdot 1 + 3 \cdot 0 \cdot (-1) + 2 \cdot 1 \cdot 1]/6 = 1$

The linear space spanned by $\Phi_l^{[3,0]},\ \Phi_l^{[2,1]},\ \Phi_l^{[1,2]},\ \Phi_l^{[0,3]}$:

$$\{3\} + \{2,1\} + \{1,1,1\}$$

$$\{3\}:\ \frac{1}{\sqrt{2}}(\Phi_l^{[3,0]} + \Phi_l^{[0,3]})\,, \qquad \{1,1,1\}:\ \frac{1}{\sqrt{2}}(\Phi_l^{[3,0]} - \Phi_l^{[0,3]})\,,$$

$$\{2,1\}:\ \begin{pmatrix} \Phi_l^{[2,1]} \\ \Phi_l^{[1,2]} \end{pmatrix}.$$

# Symmetry of the vibrational wave function

$$\Psi_v = \Phi_1(q_1)\Phi_2(q_2)\Phi_3(\vec{q}_3)\Phi_4(\vec{q}_4)$$

The linear space of all vibrational DoFs:

$$\mathcal{L} = \mathcal{L}_1 \otimes \mathcal{L}_2 \otimes \mathcal{L}_3 \otimes \mathcal{L}_4.$$

This yields a reducible representation with the character

$$\chi_v(P) = \chi_1(P)\chi_2(P)\chi_3(P)\chi_4(P).$$

The normal mode 1 is fully symmetric, $\chi_1(P) = 1$.
The 2nd normal mode (incl. inversion!) is antisymmetric, $\chi_2(P) = (-1)^{\varpi_P v_i}$; $\{\lambda\} = \{3\}$ for even $v_i$ and $= \{1,1,1\}$ for odd $v_i$.
The wave functions of modes 3 and 4 can have the symmetry $\{3\}$, $\{2,1\}$, $\{1,1,1\}$. The vibrational w.f. has the symmetry $\{\lambda_2\} \otimes \{\lambda_3\} \otimes \{\lambda_4\}$.

$$\{3\} \otimes \{3\} = \{1,1,1\} \otimes \{1,1,1\} = \{3\}, \quad \{1,1,1\} \otimes \{3\} = \{1,1,1\},$$

$$\{2,1\} \otimes \{3\} = \{2,1\} \otimes \{1,1,1\} = \{2,1\},$$

$$\{2,1\} \otimes \{2,1\} = \{3\} + \{2,1\} + \{1,1,1\}.$$

# Rotational ⊗ vibrational ⊗ electronic wave function

$$\chi_{rve}(P) = \chi_r(P)\chi_v(P)\chi_e(P)$$

For the ground state of $NH_3$, $\chi_e(P) \equiv 1$, and

$$\{\lambda_{rve}\} = \{\lambda_r\} \otimes \{\lambda_v\}$$

All symmetry types are possible, but an additional restriction arises from the statistics of nuclear spins (Fermi-Dirac for $NH_3$, $s = \frac{1}{2}$, Bose-Einstein for $ND_3$, $s = 1$).

# General theory for spin statistics in polyatomic molecules

Assume a molecule containing $n$ identical nuclei (bosons or fermions) with spin $s$.

$$\sum_{j=1}^{n} \hat{\mathbf{s}}_j = \hat{\mathbf{I}}$$

Assume that the rovibronic wave function $\Psi_{rve}$ transforms according to an IR $\{\lambda\}$ of the $S_n$ group, $d_{\{\lambda\}}$ being the dimension of this IR. This means that the $d_{\{\lambda\}}$ rovibronic functions transform as

$$\hat{P}\Psi_j = \sum_{j'=1}^{d_{\{\lambda\}}} \tau_{jj'}^{\{\lambda\}}(\hat{P})\Psi_{j'}$$

The complex-conjugate functions:

$$\hat{P}\Psi_j^* = \sum_{j'=1}^{d_{\{\lambda\}}} \tau_{jj'}^{\{\lambda\}\,*}(\hat{P})\Psi_{j'}^*$$

Since the characters of $S_n$ are real, matrices $\tau_{jj'}^{\{\lambda\}\,*}(\hat{P})$ comprise an IR corresponding to the same $\{\lambda\}$.

We always can choose a unitary transformation:

$$\forall \hat{P}: \quad \sum_{i=1}^{d_{\{\lambda\}}} \tau_{ij}^{\{\lambda\}\,*}(\hat{P})\tau_{ik}^{\{\lambda\}}(\hat{P}) = \delta_{jk}$$

$\Psi_j$'s depend on electronic, vibrational, and rotational coordinates and transform according to an IR $\tau^{\{\lambda\}}$.

Integer $s$, bosonic nuclei.

We choose nuclear spin functions $\mathrm{X}_j$'s transforming under permutations of nuclear spins according to $\tau^{\{\lambda\}\,*}$. Then for the full (coordinate-spin) w.f.

$$\Psi_{rve,spin} = \frac{1}{\sqrt{d_{\{\lambda\}}}} \sum_{j=1}^{d_{\{\lambda\}}} \Psi_j \mathrm{X}_j$$

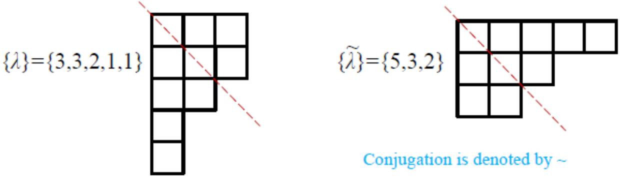
$$\hat{P}\Psi_{rve,spin} = \frac{1}{\sqrt{d_{\{\lambda\}}}} \sum_{j=1}^{d_{\{\lambda\}}} \tau_{jk}^{\{\lambda\}}(\hat{P})\tau_{jj'}^{\{\lambda\}\,*}(\hat{P})\Psi_k \mathrm{X}_{j'} = \frac{1}{\sqrt{d_{\{\lambda\}}}} \sum_{k=1}^{d_{\{\lambda\}}} \Psi_k \mathrm{X}_k =$$

$= \Psi_{rve,spin}, \quad$ i.e., the w.f. is bosonic.

## Half-integer *s*, fermionic nuclei.

$\{1,1,\ldots,1\} \otimes \{\lambda\} = \{\tilde{\lambda}\}$ is an IR corresponding to a conjugate Young diagarm:

Conjugate diagrams: rows ↔ colums, or, equivalently, reflection with respect to the diagonal ╲ .



Conjugation is denoted by ~

$$d_{\{\lambda\}} = d_{\{\tilde{\lambda}\}}$$

One-dimensional antisymmetric representation:

$$\hat{P}\psi_{\{1,1,\ldots,1\}} = (-1)^{\varpi_P}\psi_{\{1,1,\ldots,1\}}.$$

where $\varpi_P$ is a number of pairwise permutations in $\hat{P}$ (odd or even).

For fermionic nuclei, spin functions $\mathrm{X}_j$:

$$\hat{P}\mathrm{X}_j = \sum_{j'=1}^{d_{\{\lambda\}}} \tau_{jj'}^{\{\tilde{\lambda}\}\,*}(\hat{P})\mathrm{X}_{j'} = (-1)^{\varpi_P} \sum_{j'=1}^{d_{\{\lambda\}}} \tau_{jj'}^{\{\lambda\}\,*}(\hat{P})\mathrm{X}_{j'}$$

It follows from the unitarity of $\tau^{\{\tilde{\lambda}\}}$ that the whole w.f. has the fermionic symmetry:

$$\hat{P} \sum_{j=1}^{d_{\{\lambda\}}} \frac{\Psi_j \mathrm{X}_j}{\sqrt{d_{\{\lambda\}}}} = (-1)^{\varpi_P} \sum_{j=1}^{d_{\{\lambda\}}} \frac{\Psi_j \mathrm{X}_j}{\sqrt{d_{\{\lambda\}}}}$$

# Spin functions of three identical particles

Notation: $|(I_{12})IM_I\rangle$, where $I_{12}$ = intermediate coupling moment.

$[\hat{P}, \hat{I}_\zeta] = 0,\ [\hat{P}, \hat{\mathbf{I}}^2] = 0,\ \ [\hat{P}, \hat{\mathbf{I}}^2_{12}] \neq 0$ $\qquad (\zeta$ = lab.axis).

$I,\ M_I$-manifolds with different $I_{12}$ can be classified w.r.t. $\{\lambda\}$.

| $s$ | $I$ | $I_{12}$ | $\{\lambda\}$ |
|---|---|---|---|
| 0 | 0 | 0 | $\{3\}$ |
| $\frac{1}{2}$ | $\frac{3}{2}$ | 1 | $\{3\}$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | 1 | $\{2,1\}$ |
| $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | $\{2,1\}$ |

| $s$ | $I$ | $\sum \lvert(I_{12})\rangle$ | $\{\lambda\}$ |
|---|---|---|---|
| 1 | 3 | $\lvert(2)\rangle$ | $\{3\}$ |
| 1 | 2 | $\lvert(2)\rangle$ | $\{2,1\}$ |
| 1 | 2 | $\lvert(1)\rangle$ | $\{2,1\}$ |
| 1 | 1 | $\frac{\sqrt{5}}{3}\lvert(0)\rangle + \frac{2}{3}\lvert(2)\rangle$ | $\{3\}$ |
| 1 | 1 | $\frac{2}{3}\lvert(0)\rangle - \frac{\sqrt{5}}{3}\lvert(2)\rangle$ | $\{2,1\}$ |
| 1 | 1 | $\lvert(1)\rangle$ | $\{2,1\}$ |
| 1 | 0 | $\lvert(1)\rangle$ | $\{1,1,1\}$ |

# Nuclear spin states for $NH_3$ and $ND_3$

## $NH_3$

| $\{\lambda\}_{rve}$ | $\{\tilde{\lambda}\}_{ns}$ | $I$ |
|---|---|---|
| $\{3\}$ | $\{1,1,1\}$ | N/A |
| $\{2,1\}$ | $\{2,1\}$ | $\frac{1}{2}$ |
| $\{1,1,1\}$ | $\{3\}$ | $\frac{3}{2}$ |

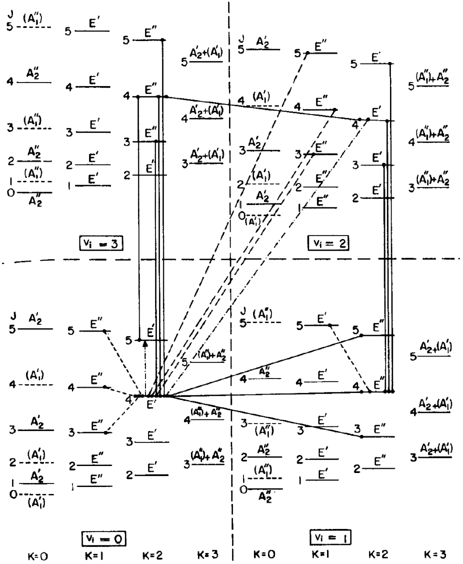
## $ND_3$

| $\{\lambda\}_{rve}$ | $\{\lambda\}_{ns}$ | $I$ |
|---|---|---|
| $\{3\}$ | $\{3\}$ | 3, 1 |
| $\{2,1\}$ | $\{2,1\}$ | 2, 1 |
| $\{1,1,1\}$ | $\{1,1,1\}$ | 0 |

A level with a total nucl. spin $I$ is $(2I+1)$-fold degenerate, $M_I = -I, -I+1, \ldots, I-1, I$.

I. Solid lines: Allowed transitions with $\Delta K = 0$, $\Delta v_i$ odd, $\Delta J = 0, \pm 1$.

II. Dashed lines: transitions allowed due to vibrational-rotational coupling, $\Delta K \neq 0$, $\Delta v_i$ even, $\Delta J = 0, \pm 1$.



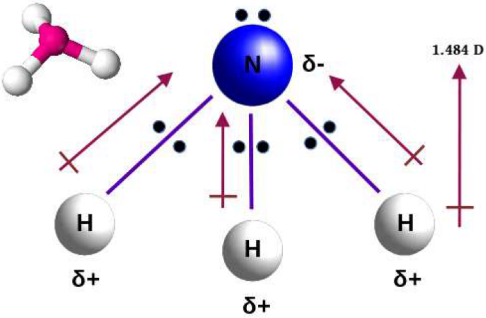
III. Dot-dashed lines: Two-photon transitions (or allowed in electric field), $\Delta K = 0$, $\Delta v_i$ even, $\Delta J = 0, \pm 1, \pm 2$.

$A_1 \sim \{3\}$

$A_2 \sim \{1, 1, 1\}$

$E \sim \{2, 1\}$

# Static dipole moment of ammonia



$$1\ \mathrm{D} \approx 0.39343\, e a_B$$

Permutation of one pair of H atoms changes the direction of $z$-axis, hence, changes $\mu_z$ to $-\mu_z$. The operator of dipole moment has the symmetry $\{1, 1, 1\}$ against permutations.

$$\{\lambda\}_{in} \otimes \{1, 1, 1\} = \{\lambda\}_f$$

# Allowed transitions

States with spatial $\{3\}$ are absent in $NH_3$ (no spin w.f. with $\{1, 1, 1\}$ for $s = \frac{1}{2}$).
These states are present in $ND_3$, but there are no transitions between the states with $\{3\}$ and $\{1, 1, 1\}$, because IR and MW transitions conserve the total nuclear spin of three H.
Therefore, transitions between the double-degenerate states ($\{2, 1\}$) are allowed: $\{2, 1\} = \{2, 1\} \otimes \{1, 1, 1\}$, and $\Delta v_i$ being odd.
From the Wigner–Eckart theorem:

$$\Delta J = 0,\ \pm 1, \qquad \Delta K = 0.$$

The lowest frequencies are for $v_i = 0 \longleftrightarrow v_i = 1$.

# Forbidden transitions

The underlying symmetry is broken if we take into account the coupling between the vibrational and rotational DoFs. This allows for (weak) transitions with even $\Delta v_i$ and odd $\Delta K$; $\Delta J = 0,\ \pm 1.$

## Two-photon transitions

$$\{1,1,1\} \otimes \{1,1,1\} = \{3\}$$

For two-photon processes, $\Delta v_i$ is even.
From the Wigner–Eckart theorem:

$$\Delta J = 0,\ \pm 1\ \pm 2, \qquad \Delta K = 0.$$

These transitions can be also activated by an external electric field, mixing even and odd $v_i$, as single-photon transitions.

# Molecular symmetry group

In many molecules, potential barriers between different configurations are impenetrable. Example: $CH_3Cl$. In that case, the levels with different types of symmetry w.r.t. permutations of identical nuclei are degenerate. Then the levels are classified according to the molecular symmetry group, i.e., the point group of symmetry of the equilibrium configuration of a molecule.

D. M. Jonas, Spin statistics: An error in Landau and Lifschitz' *Quantum Mechanics*. J. Chem. Phys. **90**, 5563 (1989).